EXPLORING THE NATURE OF THE ADIABATIC APPROXIMATION IN STUDIES OF PROTONATED WATER CLUSTERS

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Proton transport is ubiquitous, insights into its underlying mechanism and manifestation in vibrational spectroscopy are important for a variety of scientific fields. One way to probe these motions is through the studies of protonated water clusters, $H^+(H2O)_n$. Gaining insights of the interplay between the OH stretch of one of the hydrogen atoms on the hydronium core and the OO vibration involving the oxygen atom in its coordinated water molecule is critical in understanding proton transport through these hydrogen bonded networks. It has been shown theoretically and experimentally that the ability of a proton to undergo transfer through the hydrogen-bonded network is highly influenced by the distance between the donor and acceptor oxygen atoms.

The simplest model that incorporates this coupling is based on an adiabatic treatment of the Hamiltonian in which the OH and OO stretches are described by two harmonic oscillators which are coupled through a cubic term in the potential. This model has been shown to replicate experimental spectral features of these protonated water clusters. This raises questions of why such a simple model works so well and how the adiabatic treatment, or inclusion of higher order terms in the potential and dipole surface affect the results. To investigate these questions, we have introduced higher order terms in the potential and dipole surfaces within an adiabatic treatment, where we first add only higher order terms to the potential and then add the higher order terms of both the potential and the dipole surface. In addition, we have considered the effects of the adiabatic treatment itself by implementing a full 2D calculation for describing the OO and OH stretching motions. In comparing the results of the adiabatic treatment to experiment, the cubic harmonic model, and the full 2D calculation, the leading correction comes from the higher order terms in the potential. The calculation of intensity shows small, yet notable, corrections from higher order terms in the dipole moments.